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Effect of doping on formation of solid state battery in lithium vanadate

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Abstract : The d.c. electric field effect on ferro-electric lithium vanadate doped with different concentrations of neodymium oxide above the Curie temperature shows the formation of solid state battery. The emf and current generated was measured between two electrodes stuck into the fused samples of Nd-doped lithium vanadate ; after d.c. electric field of about 1 KV cm^{-1} was once applied at high temperature above Curie temperature and then taken off. The generated emf and current depend on temperature as well as on dopant concentrations. A drastic change in emf and current is observed at phase transition temperature. The emf decays with time but decay constant is quite large. The magnitudes of emf and current at Curie temperature are found to increase significantly, when dopant concentration is increased up to 0.5 mol % Nd_2O_3, however decrease for higher concentrations. The Curie temperature of lithium vanadate decreases with increase of Nd concentration.

Keywords : Solid state battery (SSB), phase transition temperature, lithium vanadate, neodymium oxide.

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1. Introduction

The formation of solid state battery (SSB) was first time reported by Sawada *et al* (1958, 1961) during the experimental study of electric field effect on the ferro-electricity of the KNO_3 crystals. Ishibashi *et al* (1969) observed the emf of about one volt between two electrodes stuck into the fused KNO_3 crystal after switching off d.c. electric field (about 1 kV cm^{-1}) which was applied at high temperature. Recently, a great deal of interest has been shown in lithium ion conductors which are useful for power source applications. Several solid electrolytes with conducting species such as Na^+, Li^+, Cu^+ and Ag^+ ions have been investigated. It was reported by Pistoia *et al* (1984) that the solid solutions of ($Li_{1+x}V_2O_5$) can be used as cathode for high rate secondary lithium batteries. Similarly, it was studied by Kikkawa *et al* (1987) that the solid solution of $Ti(S_{1-x}-Se_x)_2$ could be used as a cathode for lithium battery. Suryavanshi and Chavan (1987) investigated the

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formation of SSB in KVO_3 and $NaVO_3$ and concluded that the response of SSB is satisfactory above Curie temperature. Recently, Patil *et al* (1989) reported the formation of SSB of KVO_3 doped with Dy_2O_3.

In this investigation, the formation of SSB by the lithium vanadate doped with different concentrations of neodymium oxide is reported.

2. Experimental

Lithium vanadate was prepared by usual ceramic technique reported by Feigelson *et al* (1972). The lithium carbonate used was preheated at 200°C for 2 hr before weighing, in order to minimize the moisture. The dried powder was then weighed and blended throughly with V_2O_5. The mixture was slowly heated in platinum crucible to a temperature range 700-750°C depending on the composition to melt the mass. The molten mass was held at this temperature for 5 hr inside globar furnace and then cooled to room temperature.

The Nd additive used was a specpure Nd_2O_3 of purity 99.9% (John Baker Inc, Colorado, USA). The samples were prepared by weighing Nd_2O_3 in different percentage from 0.05 to 5 mol % in $LiVO_3$. Every batch was subsequently dry mixed and then mixed wet with ethyl alcohol in an agate mortar. After the alcohol was completely evaporated, the batches were heated in platinum crucible to a temperature range 900-950°C depending on the composition to melt the mass. The molten mass was held at this temperature for about 5 hr inside globar furnace and cooled to room temperature. The samples were then ground to pass a 120 mesh sieve. X-ray powder diffractometer traces for undoped and doped $LiVO_3$ ceramics were obtained using Philips X-ray powder diffractometer with CuK_α radiations to confirm structures of prepared samples.

The pellets were pressed at 7.6×10^7 kg m^{-2} pressure using hydraulic press, in the form of discs (diameter 1 cm and about 0.1 cm thick) and were sintered on platinum foil at 500°C for 3 hr inside a globar furnace. The two opposite faces of each pellet were polished and silvered with air-drying silver paste to achieve good electrical contacts.

The experimental set-up consisted of a globar furnace, an electronically regulated power supply, a digital DC microvoltmeter with a pico-ammeter adaptor and a temperature controller arrangement. A d.c. electric field of about 1 kV cm^{-1} was applied to the pellets kept in pellet-holder having stainless steel electrodes and at a temperature of 500°C for a short time. The pellets were fused and the d.c. electric field was removed. Immediately, the generated emf and current produced through the samples were measured while cooling the samples. Similar procedure was repeated to study the decay of emf at constant temperature.

3. Results and discussion

The generated emf and current were measured while cooling the pellets of ferroelectric lithium vanadate doped with different concentrations (0 to 5 mol of neodymium oxide and are shown in Figure 1 and Figure 2 respectively.

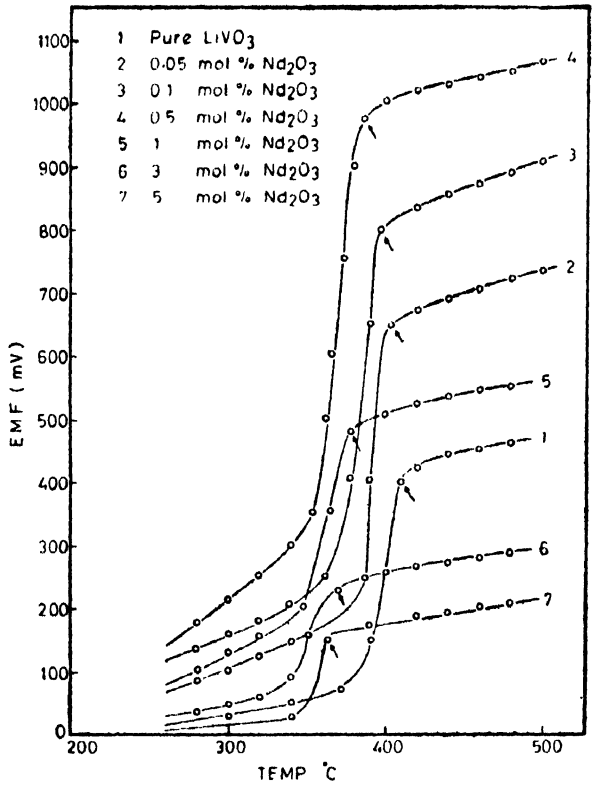

Figure 1. Temperature dependence of emf for $LiVO_3$ ceramics with different Nd_2O_3 concentrations (mol %).

It is clear from Figures 1 and 2 that the generated emf and current not only depend on temperature but also on dopant concentrations. A drastic change in emf and current observed at 409°C indicates the Curie temperature for pure $LiVO_3$. This Curie temperature is in good agreement with that reported previously by Patil *et al* (1988), which has also been confirmed by DTA.

The addition of Nd_2O_3 to $LiVO_3$ shows noticeable shift in the Curie temperature to lower temperature in agreement with the results obtained by previous investigators for SBN doped with rare-earth ions (Pr^{3+} and Nd^{3+}) (Kuroda and Kubota 1980), and for $BaTiO_3$ doped with Nd and Mn (Murugaraj and Kutty 1985). The Curie temperature decreases linearly with increase in concentration of Nd_2O_3, which has been confirmed during the experimental study of measurement of dielectric constant by us (Patil *et al* 1990).

The magnitude of emf and current at phase transition is found to increase when dopant concentration is increased up to 0.5 mol % Nd_2O_3 which however, decreases for higher concentrations.

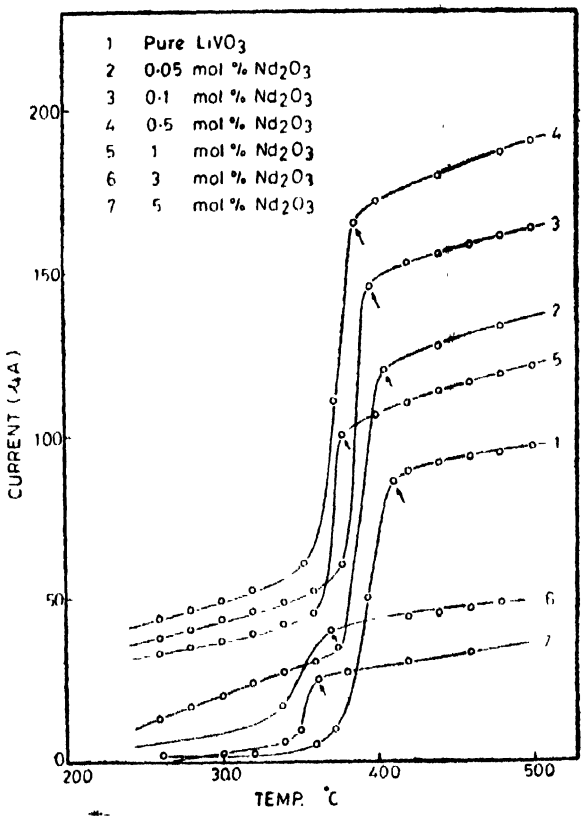

Figure 2. Temperature dependence of current for $LiVO_3$ ceramics with different Nd_2O_3 concentrations (mol %).

The decay of emf with time at constant temperature (500°C) is shown in Figure 3.

It is observed that the decay constant is quite large. The decay time required to fall in emf (E) to its ($1/E$)-th values are calculated from the graph of decay of emf with time for all samples (Figure 3) and are summarized in Table 1.

Table 1 reveals that the fall of emf to its ($1/E$)-th value depends on dopant concentrations. It increases up to 0.5 mol % Nd_2O_3 and then decreases for higher concentrations.

The typical curve for $LiVO_3$ doped with 0.5 mol % Nd_2O_3 when electrodes were short-circuited, is presented in Figure 4.

The Figure 4 shows that if the two electrodes were short-circuited and re-opened, the emf gradually recovers to the same value of voltage as obtained without any short-circuitry.

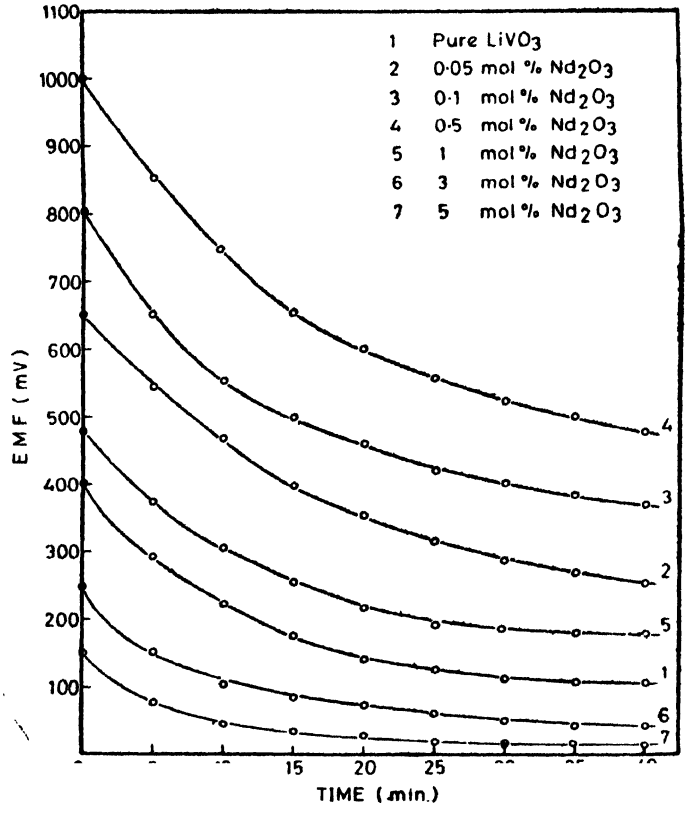

Figure 3. Decay of emf for $LiVO_3$ ceramics with different Nd_2O_3 concentrations (mol %) at 500°C.

Table 1. Decay time required to fall in emf (E) to its ($1/E$)th value for rdifferent samples of $LiVO_3$.

Nd_2O_3 content mol %	Decay time (min)
0	208
0.05	420
0.1	578
0.5	698
1	312
3	119
5	72

The illumination result is the effect of d.c. electric field on ferroelectric lithium vanadate doped with neodymium oxide above Curie temperature, shows the formation of solid state battery. It is observed that some chemical reaction is taking place and a solid state battery is formed.

The phenomenon may be explained as follows :

By applying d.c. electric field about 1 kV cm^{-1} once across the samples above Curie temperature for short time, $LiVO_3$ gets fused into alkali metal positive ions and negative radicals of vanadate $(VO_3)^-$. The alkali metal positive ions become

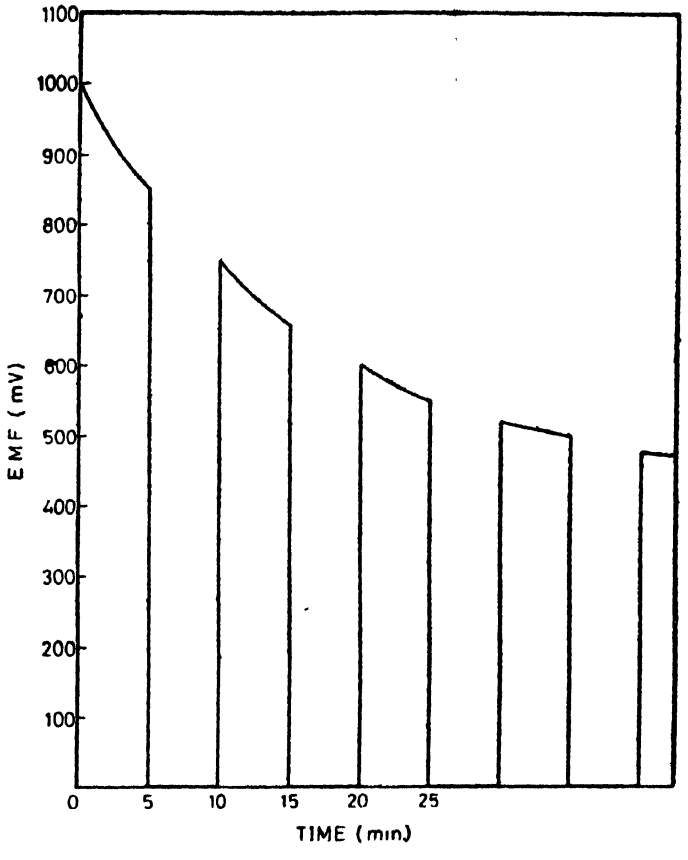

Figure 4. Decay of emf at 500°C for 0.5 mol % Nd_2O_3 doped $LiVO_3$.

neutral by removing electrons from cathode (cathodic reduction). The negative vanadates become neutral by accepting electrons at anode (anodic oxidation). The neutral VO_3 radicals are unstable, so they decompose into VO_2 and O_2. VO_2 remains as residue and O_2 gets liberated at the anode. Thus the battery gets charged. After short time of charging, the d.c. electric field is shut off and then the discharging of battery takes place. The chemical reaction during the charging is reversed in discharge process. During this process VO_2 and part of O_2 combine

by receiving electrons to form negative radicals $(VO_3)^-$. This negative radicals react with positive alkali metal ions to form alkali metal vanadates.

In the present study, the formation of battery of $LiVO_3$ doped with different concentrations of Nd_2O_3 may be explained as follows :

When d.c. electric field of about 1 kV cm^{-1} was once applied across the sample—pellets of $LiVO_3$ doped with different concentrations of Nd_2O_3 at 500°C for a short time, part of it gets decomposed into (Li+Nd) and O_2 and VO_2 remains as residue, O_2 gets liberated at positive terminal as a gas. (Li+Nd) radicals get deposited near the negative terminal. Therefore, we obtain a battery of

Steel, $(Li+Nd)/LiVO_3 : Nd/VO_2 ; O_2$, Steel.

4. Conclusion

As a result of this investigation the following conclusions may be drawn :

(i) At very high temperature i.e. above Curie temperature, the effect of d.c. electric field on pure and doped $LiVO_3$ shows the formation of SSB.

(ii) Response of the SSB is satisfactory above the Curie temperature.

(iii) The addition of Nd_2O_3 to $LiVO_3$ shows noticeable shift in the Curie temperature to lower temperature.

(v) The magnitudes of the emf and current depend on the doping concentrations. They increase up to 0.5 mol % of Nd_2O_3 but decrease for higher concentrations.

(vi) The emf decays with time but decay constant is quite large.

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